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Use of the Second, Third and Fourth Gas—Solid Virial Coefficients to the Problem of Estimating Adsorptive Properties of Adsorbents

Zastosowanie drugiego, trzeciego i czwartego współczynnika wiriału gaz—ciało stałe do celów badania własności adsorbentów

Применение второго, третьего и четвёртого вириальных коэффициентов в проблеме исследования адсорбционных свойств адсорбентов

INTRODUCTION

Many various physical quantities were used so far, to describe adsorptive properties of adsorbent surfaces [1]. The most often used are: the surface area, the energy of adsorption, and the volume of the surface phase, considered as the volume of where adsorption forces exist [2]. Next, the energy and the pore distribution functions, in the case of non-uniform porous adsorbent surfaces.

However, the above mentioned quantities are of a macroscopic nature. For many purposes the knowledge of microscopic properties of the adsorbent surfaces is needed, as for instance in catalytic investigations. For these purposes some new kinds of physical quantities have been introduced to describe the microscopic properties. Apart from a detailed purpose the kind of the quantities used in the microscopic description depends upon the adsorption model assumed.

Consider for instance the simplest case of the fully uniform adsorbent surfaces. Then, the parameters describing the potential energy of adsorption are the most usual quantities, when assuming additionally the non-localized adsorption. On the other hand, when the localized adsorption is assumed then the number of the adsorption sites, their energy of adsorption, and their distribution on the adsorbent surface are the most usual set of the quantities.

However, it is not necessary to determine the adsorption model which is appropriate for a given adsorption system. Both the localized, and the non-localized adsorption are ideal cases only, the real adsorption systems being only their approximations. Thus, the model of adsorption should be treated as a basic idea of the description formalism rather, then an accurate picture of an adsorption process.

Recently we have proposed a new kind of the microscopic description of the adsorptive properties of the adsorbent surfaces, based on the model of the non-localized adsorption [3]. The experimental data, which are needed in this description can be easily and accurately obtained by gas chromatography [4]. These are the second, and the third gas-solid virial coefficients. From their temperature dependence one can extract all the quantities used in the microscopic description proposed by us.

The purpose of this paper is to show, how the gas-solid virial coefficients can be used to evaluate the microscopic quantities, used generally in the description based on the model of localized adsorption. Moreover, some new possibilities will be discussed, concerning a more detailed microscopic descriptions, when assuming the localized adsorption.

THEORETICAL

The virial treatment of the physical adsorption of gases was successfully used to describe properties of many adsorption systems [5]. However, the theoretical investigations based on this description formalism, which have been made so far, concern the case of non-localized adsorption only. The adsorption systems with localized particles were considered by using other description formalisms [6], which have a number of serious weaknesses in comparison with the virial formalism. For instance, there exist difficulties to take into account the correlations between the adsorbed particles.

The reason, for which the virial treatment was not used in descriptions of the localized adsorption systems, seems to be rather of a historical nature. The virial formalism was previously used in descriptions of bulk phases, consisting of non-localized particles.

Next, it was in a natural way extended to describe the systems with non-localized particles, being in an external field, which in particular may be provided by the adsorbent surface [7—11].

In the most general statistical treatment of physical adsorption, the adsorbent and the adsorbate are treated together, and the mobility of the adsorbent molecules is allowed [12]. The grand partition function is then evaluated for the mixture, consisting of the adsorbent and adsorbate molecules. However, for majority of the adsorption systems containing the solid adsorbent the assumption can be made, that the adsorbent molecules form an inert structure, which is not affected by the presence of adsorbate molecules. Then, the theoretical description reduces to the description of the adsorbate molecules included in the volume V, and being in the presence of an external field due to the inert structure.

The average number N of the adsorbed molecules is then equal [5].,

$$N=(\bar{N}-\bar{N}^{*})=Z\left(\frac{\partial\ln(\Theta/\Theta^{*})}{\partial Z}\right)_{V,T} \tag{1}$$

where $\bar{N}$ and $\bar{N}^{*}$ are the average numbers of adsorbate particles included in the volume V at the temperature T, in the presence and in the absence, respectively, of the external field provided by the inert structure.

Consequently Θ and Θ^{*} are the grand partition functions for the adsorption systems under the two above mentioned conditions. Thus, we have,

$$N=\sum_{i\geqslant 1} i\,(\beta_i-\beta_i^{*})\,Z_i \tag{2}$$

where β_i and β_i^{*} are cluster-type integrals dependent upon appropriate configuration integrals Z_i, and Z_i^{*}. For example,

$$\begin{gathered}\beta_1=Z_1\\ 2!\,\beta_2=[Z_2-Z_1^2]\\ 3!\,\beta_3=[Z_3-3Z_1Z_2+2Z_1^3]\end{gathered} \tag{3}$$

and

$$\begin{gathered}\beta_1^{*}=Z_1^{*}\\ 2!\,\beta_2^{*}=[Z_2^{*}-(Z_1^{*})^2]\\ 3!\,\beta_3^{*}=[Z_3^{*}-3\,Z_1\,Z_2+2\,(Z_1^{*})^3]\end{gathered} \tag{4}$$

Consider now the case of the external adsorption field ε, being an uniform one for the whole adsorption space V, i.e. $\varepsilon(\mathbf{r})=\varepsilon_o$ for $\mathbf{r}\in V$. Assuming additionally that the total interaction energy between the adsorbed particles can be assumed to consist of pair interactions only, we may write,

$$\beta_1=\left[\exp\left(\frac{-\varepsilon_o}{kT}\right)\right]\int_V dr_1$$

$$2!\,\beta_2=\left[\exp\left(\frac{-2\,\varepsilon_o}{kT}\right)\right]\iint_V f_{12}\,dr_1\,dr_2 \tag{5}$$

$$3!\,\beta_3 = \left[\exp\left(\frac{-3\varepsilon_o}{kT}\right)\right]\cdot\iiint\limits_V (3f_{12}\,f_{23} + f_{12}\,f_{23}\,f_{31})\,d\mathbf{r}_1\,d\mathbf{r}_1\,d\mathbf{r}_1$$

where

$$f_{ij} = \left\{\exp\left[\frac{U(\mathbf{r}_i,\mathbf{r}_j)}{-kT}\right] - 1\right\} \tag{6}$$

and $U(\mathbf{r}_i, \mathbf{r}_j)$ is the interaction energy between two particles, whose centers of masses are at the points $\mathbf{r}_i$ and $\mathbf{r}_j$. Comparing (3) and (4) we get

$$\beta_i{}^* = \left[\exp\left(\frac{\varepsilon_o}{kT}\right)\right]\beta_i \tag{7}$$

For the most interesting case of the positive adsorption $\varepsilon_o < 0$, and even for simple gases on typical adsorbents $\left[\exp\left(\frac{\varepsilon_o}{kT}\right)\right] \approx 10^{-5}$ at room temperatures. For this reason we shall later neglect $\beta_i{}^*$ in comparison with β_i, for the region of the adsorption forces. Next, it is rather obvious that the integral $\int\int\int f_{12}f_{23}f_{13}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3$ should be much smaller than the integral $\int\int\int f_{12}f_{23}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3$ what follows from the form of the function f_{ij}. For this reason we shall approximate β_3 by the following value,

$$\beta_3 = \frac{1}{2}\left[\exp\left(\frac{-3\varepsilon_o}{kT}\right)\right]\iiint\limits_V f_{12}\,f_{23}\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \tag{8}$$

Now we would like to explain the connection between the quantities used in the microscopic description based on the model of localized adsorption, and the coefficients β_i.

For this purpose we remark that in the case of the systems with localized particles, the configuration integrals Z_N (N, V, T) are replaced by the expressions $\sum\limits_s\left[\exp\left(\frac{E_s}{-kT}\right)\right]$ where the summation is running over allowable positions of N molecules on ω points, E_s being the total potential energy connected with the s-th position. Of course in the localized adsorption systems ω means the number of the adsorption sites, each of whose having the energy of adsorption equal to ε_0.

Thus, to evaluate β_i for such localized systems we must replace the integration with respect to $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ by the summation over the allowable positions of the vectors $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$. In this way we get,

$$\beta_1 = \omega\left[\exp\left(\frac{-\varepsilon_o}{kT}\right)\right] \tag{9}$$

Next assume that for every adsorption site, there exist ζ_0 nearest neighbours — adsorption sites, such that there is remarkable interaction between two adsorbate molecules occupying two nearest adsorption sites. With this assumption we may write,

$$\beta_2 = \frac{1}{2}\left[\exp\left(\frac{-2\,\varepsilon_o}{kT}\right)\right] \omega\,\xi_o \left[\exp\left(\frac{U_o}{-kT}\right) - 1\right] \tag{10}$$

where U_0 is the average interaction energy between two adsorbate molecules, adsorbed on two nearest adsorption sites.

To evaluate β_3 we suppose that for two adsorbate molecules adsorbed on two nearest adsorption sites, there exist on average ζ_1 nearest neighbours — adsorption sites acceptable for a single third molecule, so that there are remarkable interactions between the third and one of the two above mentioned molecules. Denote by U_1 the average energy of interaction between the single third molecule and one of the two molecules mentioned above. Then we have,

$$\beta_3 = \frac{1}{2}\left[\exp\left(\frac{-3\,\varepsilon_o}{k\,T}\right)\right] \omega\,\xi_o\,\xi_1 \cdot \left[\exp\left(\frac{U_o}{-kT}\right) - 1\right]\left[\exp\left(\frac{U_1}{-kT}\right) - 1\right] \tag{11}$$

Of course, in the case of planar (wide porous), solid surfaces there should be,

$$\zeta_1 = \zeta_0 - 1 \tag{12}$$

Because of the abridgements introduced by the existence of pores it may so happen, that ζ_1 will be different from $(\zeta_0 - 1)$. Thus, the value ζ_1 may be treated as a kind of information concerning the structure of adsorbents. Now we want to explain, how the above discussed microscopic quantities can be extracted from the experimental values β_1, β_2 and β_3.

From the experimental plot $\ln\beta_1$ against $\frac{1}{T}$ one can obtain both ε_0 and ω, as connected with the slope and the intercept of this line, respectively. After inserting these values into the expressions for β_2, one gets β_2 as a two-parameter function of temperature, with meanwhile uknown parameters ζ_0 and U_0. These parameters can be found by using the "best-fit" procedure for β_2 as expressed by eq. (10), with respect to its values found experimentally.

Next, using ε_0, ω, ζ_0 and U_0 in the expression for β_3, one gets β_3 as a two-parameter function of temperature. The parameters ζ_1 and U_1 can be found in the analogical way as the parameters ζ_0 and U_0.

In our opinion, the ensemble of the informations concerning ε_0, ω, ζ_0, ζ_1, U_0 and U_1, is an excellent one to describe the microscopic properties of localized adsorption systems.

EXPERIMENTAL

Recently we have discussed in detail the possibility of evaluating the coefficients β_1 and β_2 from simple chromatographic data [4].

Thus, the problem which remains, is to establish the connection between any coefficient β_n and the retention volume V_N measured in gas chromatography. Following Pierotti [12] we shall call $n(\beta_n - \beta_n^*)$ — "the $(n+1)$-th gas-solid virial coefficient". According to custom the "virial" expansions are the expansions in powers of density, while the expansion in eq. (2) is the standard expansion in the powers of activity z of the system.

However, it is well-known that the virial expansions are used in descriptions of low-density behaviour of many particle systems, where the activity may be identified with the density of the systems. This is probably the reason for which $n(\beta_n - \beta_n^*)$ are treated as the $(n+1)$ the gas-solid virial coefficients.

It has been shown in the theoretical section that β_n^* are negligible in comparison with β_n for the region of adsorbed phase, i.e. the region, where adsorption forces exist. Thus, $n\beta_n$ may be identified with the $(n+1)$-th gas-solid virial coefficient, under the condition that the integration (summation), is running only over the region of the adsorbed phase. Let's divide now the total adsorbate volume V into the volume V_s of the adsorbed phase, and the volume V_f of the free gas phase, i.e. $\varepsilon(\mathbf{r}) = 0$ for $\mathbf{r} \in V_f$. Let ϱ_1 and ϱ_0 denote the concentrations of the adsorbate in the zones V_s and V_f, respectively, Then, there exists a simple relation between the retention volume V_N and the quantities V_s, ϱ_1 and ϱ_0 (13).

$$V_N = FV_S \frac{\partial \varrho_1}{\partial \varrho_0} \tag{13}$$

Above F, there is the so-called "James-Martin compressibility factor" connected with the measurement conditions.

Assuming that $\varrho_1 = \frac{N}{V_S}$ and that $z = \varrho_0$ we get:

$$V_N = F \sum_{l \geqslant 1} l^2 \beta_l \varrho_0^{(l-1)} \tag{14}$$

The reason, for which we can replace z by ϱ_0 is the following one. Because of the strong adsorption forces, one gets considerable densities ϱ_1 even at very small densities ϱ_0 in the free gas phase. The activity z is the same both for the adsorbed, and for the free gas phase. Thus, even at high densities in the adsorbed phase, its activity can be replaced by the density in the free gas phase.

The theoretical and experimental problems concerning the determination of the function $V_N = V_N(\varrho_0)$ have been in detail described by Conder. Therefore, we shall here describe only the conditions, in which our measurements were performed.

We used chromatographic column 2 m long, containing 4,00 g silicagel. To plot $V_N = V_N(\varrho_0)$ we used sample sizes being equal; 0,2 μl, 0,3 μl, 0,4 μl, 0,5 μl, and 1,0 μl, respectively. We have found that the concentrations of solute in our chromatographic column, obtained with these sample sizes vary from about 10^{-5}, to about 10^{-4} mole/l.

The measurements have been performed by means of the Polish apparatus "Chromatoprep N-502", with caterometer as detector used. As the carrier gas — hydrogen was used with flow rate about 50 ml/min.

Reagents: Silicagel — produced by Suchardt in Muenchen, West Germany, (mesh — 80/120), Carbon tetrachloride — produced by P.O.Ch. Gliwice, Poland.

Table 1. Results of our measurements, made by using 4,00 g of the Suchardt's silicagel

in °C Temperature	β_1 in 1	$4\beta_2$ in 1^2/mole	$9\beta_3$ in 1^3/mole^2
90,4	0,19741	−128,769	133,460
100,0	0,14007	− 51,345	63,496
120,7	0,10758	− 32,198	38,175
130,3	0,08317	− 20,291	21,223
130,3	0,06328	− 10,117	38,357

The values of β_n presented in this table concern the region of the adsorbed phase only, and therefore may be related to appropriate gas—solid virial coefficients.

RESULTS AND DISCUSSION

The results of our measurements are presented in the Table No. 1. To obtain these data we approximated the experimental plots $V_N = V_N(\varrho_0)$ by a polynome of second order of the type:

$$V_n(\varrho_0,T)=\beta_1(T)+4\varrho_0\beta_2(T)+9\varrho_0^2\beta_3(T) \qquad (15)$$

By using the experimental data presented in the table No. 1 we have obtained the following values for ω, ε_0, ζ_0, and U_0:

$$\omega = 3{,}201\cdot 10^8$$

$$\varepsilon_0 = -3992 \text{ cal/mole}$$

$$\zeta_0 = 14{,}83$$

$$U_0 = -1{,}310 \text{ cal/mole}$$

The most interesting are the last two values, as describing the topological structure of adsorbent surface. One may extract additionally an interesting information about average distance r between two nearest neighbours — adsorption sites. To this purpose consider the theory of the third-order interaction, (two adsorbed molecules plus surface), in the form as developed by Sinanoglu and Pitzer [14]. Assuming the adsorbed molecules to lie at the same distance from the adsorbent surface, (i.e. neglecting oscillations effects), one gets two possible values for r, at which $U(r)=0$. These are $r \approx 0{,}95\, r_0$, or $r \approx 1{,}4\, r_0$, where r_0 is the slow-collision diameter of the adsorbate molecules in the bulk phase.

The first value must be rather excluded for the following geometrical reason. Assuming that the distance between two nearest sites from the surroudings of a one consider molecule is the same as between the considered molecule and the molecules from the surroudings, and is equal to about r_0, one gets $\zeta_0=6$ as the highest possible value for ζ_0. Thus there remains the value $r=1{,}4\, r_0$, which is equal to 8,5 Å, when using the value for r_0 obtained by Lauger [15].

Let's now consider the values ζ_1 and U_1. Unfortunately, our experimental results turned out to be not sufficiently accurate, to extract the fully quantitative informations about ζ_1 and U_1. It follows from the Table No. 1, that there is no regularity in the temperature dependence of β_3. However, the values of β_3 are sufficiently accurate to evaluate the order or the quantities ζ_1 and U_1. The most appropriate data to this purpose, are the data obtained in lowest temperature. The retention volumes obtained in this temperature are the longest, and therefore the most accurate ones.

Assuming ζ_1 to be of the first order, we get the first order too for U_1, expressed in cal/mole. For instance, by assuming ζ_1 to be equal 14,83, we get for U_1 the value $-0{,}726$ cal/mole, from the data obtained in temperature 90,4 C.

From it follows, that there are not considerable differences between the values ζ_0, U_0 and ζ_1, U_1, in the case of carbon tetrachloride adsorbed by the Suchardt's silicagel. Thus, it seems that the average diameter of pores in this adsorbent is much higher than 17 Å, which value is the maximum possible distance between two adsorption sites in the configuration of three nearest neighbours — adsorption sites.

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STRESZCZENIE

W pracy niniejszej zaproponowano nowy rodzaj opisu własności adsorbentów, oparty na założeniu adsorpcji zlokalizowanej. Pokazano, że wielkości mikroskopowe potrzebne w tym opisie można wyliczyć z zależności temperaturowej współczynników wiriału gaz—ciało stałe.

РЕЗЮМЕ

В данной работе представлен новый метод описывания свойств адсорбентов, опираясь на модели локализованной адсорбции. Доказано, что микроскопные величины необходимые при этом описании можно вычислить из температурной зависимости виральных коэффициентов газ—твёрдое тело.

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